



PATENT SPECIFICATION

NO DRAWINGS

990.744

Date of Application and filing Complete Specification: Dec. 27, 1961.

No. 46225/61.

Application made in United States of America (No. 79576) on Dec. 30, 1960.

Complete Specification Published: April 28, 1965.

© Crown Copyright 1965.

Index at acceptance:—C5 E(B1F, B1H, B2C2, B2J2, B2J4); C2 C(2B3A2, 2B3B, 2B3G5, 3A13B2A4, 3A13B2G, 3A13C7, 3A13C10C, 3C10); C5 D(6A5C, 6B12B1, 6B12G2A, 6B12M, 6B12N2, 6B12N3)

Int. Cl.:—C 07 c // C 11 d

COMPLETE SPECIFICATION

Process for producing an Alkylaryl Compound suitable for the preparation of Biologically Soft Detergent

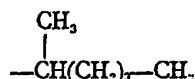
We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for the production of alkyl aromatic compounds, especially suitable for the production of detergents and other surface active agents which are biologically soft and thus subject to biological degradation during sewage treatment. More specifically, this invention relates to a process for the production of an alkylate of an aromatic compound by starting from heavy naphtha fractions containing straight chain paraffins in which the number of carbon atoms in the paraffin corresponds to the number of carbon atoms in the alkyl group of the desired aromatic alkylate to ultimately form an alkylate which when sulfonated or otherwise converted to a detergent product is subject to bacterial attack and degradation in a subsequent sewage treatment process following the use of the detergent and discharge into sewage.

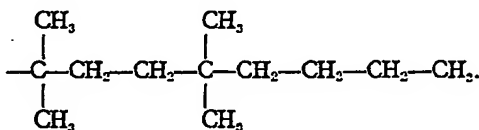
One of the major problems prevalent around centers of population throughout the world is the disposal of sewage containing even small quantities of detergents having an alkylaryl structure as the basis of the detergent molecule. These detergents produce stable foams in hard or soft waters in such large quantities that the foam clogs the sewage treatment facilities and often appear in sufficient concentration in such facilities to destroy the bacteria necessary for sufficient biological action for proper sewage treatment. One of the principal offenders of this type of detergent is the alkylaryl sulfonate detergents which, unlike the fatty acid soaps, do not precipitate when mixed with hard water containing calcium or magnesium ions in solution and since these compounds are antibacteriostatic, the detergent solution is not only carried through the sewage treatment plant in unchanged form, and having an active tendency to foam, especially when mixed with aerating devices and stirrers, a stable foam is formed which carries through the sewage treatment plant and fails to precipitate even upon further dilution with additional water, whether hard or soft. Another offender of this type of detergent is the polyoxyalkylated alkylphenols. These same synthetic detergents also interfere with the anerobic process of degradation of other materials, such as grease and thus add further to the water pollution problems. These dilute detergent solutions often enter sub-surface water currents which feed into underground water strata from which many cities draw their water supplies and the alkylaryl based detergents find their way into the water supplies drawn from water-taps in homes, factories, hospitals and schools. Occasionally these detergents turn up in sufficient quantities in tap water to make drinking water foam as it pours from the tap. Although the effluent from cities' sewage plants may be clear many tons of synthetic detergents which have resisted the sewage treatment and which have survived the bacterial action normally present in open surface streams cause the forma-

tion of large masses of foam at the bottom of weirs and dams in water streams throughout a country whose population utilized large quantities of synthetic detergents. During 1959 over 680 million kilograms of surface active agents (on the unbuilt basis, that is, exclusive of the inorganic salts added to commercial detergents) were sold in the United States. Of this quantity of synthetic detergents entering the sewage treatment facilities throughout the United States, 240 million kilograms of this was of the bacterially non-degradable (hard) synthetic alkylbenzene sodium sulfonate type of detergent.

An adequate supply of pure water, like clean air, is essential to the further growth and development in many areas of the country and to the health of millions of people throughout the world. It has been found that alkylaryl-based detergents, such as sodium alkylbenzene sulfonate, are more readily degradable by sewage bacteria if the alkyl portion of the molecule is of a simple, straight-chain configuration than if it is of a more complex branched chain structure. As an example, detergent compounds containing the alkylaryl hydrophobic group and having an alkyl side chain structure such as:



are more likely to be bacterially digested than detergents of the same chemical composition but having side chain alkyl group structures such as:



Thus, alkylaryl-based detergents in which the alkyl portion of the molecule has a structure corresponding to the straight chain structure of the alkyl group illustrated in the first of the two structures above, produce biologically soft detergents which undergo bacterial degradation in sewage treatment plants with relative ease, whereas products formed from alkylaryl hydrocarbons containing a branched chain alkyl group such as the polymethylated structure indicated in the second of the two structures illustrated above produce "hard" detergents which are much more resistant to bacterial degradation in the effluent of sewage treatment plants and appear as active detergents in the effluent of sewage treatment.

It is an object of this invention to produce alkyl aryl hydrocarbons in which the alkyl side chain attached to the aromatic nucleus is of sufficiently straight chain structure to be capable of producing biologically soft detergents by the inclusion of a suitable hydrophilic radical in the structure of the compound. Another object of this invention is to provide an alkylaryl hydrocarbon structure suitable for the production of biologically soft detergents therefrom without sacrifice in the yield of product, effectiveness of the final detergent product or its watersolubility.

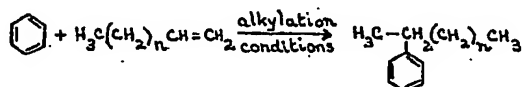
In accordance with this invention an alkylaryl compound especially suitable for the preparation of a biologically soft detergent product therefrom in which the aryl nucleus is mono-cyclic and the alkyl radical on the aryl nucleus is an alkyl group containing from 9 to 15 carbon atoms is produced by a process wherein a straight chain paraffin of at least 95% normal paraffin purity is separated from a paraffinic naphtha boiling in the range of from 125° to 250°C., by a selective separation treatment of the group consisting of molecular sieve sorption, urea adduct formation and thiourea adduct formation, the separated straight chain paraffin is converted without intentional isomerization of the straight chain structure to an olefin-acting derivative of the group consisting of mono-olefinic hydrocarbons and alkyl halides having the same carbon atom number as said straight chain paraffin and an aromatic compound selected from the group consisting of benzene, toluene, xylene, ethylbenzene, methyl-ethylbenzene and phenol is alkylated with said olefin-acting derivative to form the mono-alkylate of said aromatic compound.

The alkylaryl hydrocarbon product of this invention, herein referred to as "alkylate", provides a convenient starting material for the preparation of a wide variety of detergent products, some of which are also useful as general surface active agents in such applications as tanning agents, softening agents, handbar soaps and a

wide variety of other useful applications, in most applications of which an aqueous solution of the detergent or surface active agent enters into the sewage waste disposal system for treatment in a remote sewage treatment plant. Thus, the alkylate product of this invention may be sulfonated and neutralized with a suitable alkaline base, such as sodium hydroxide to form the so-called alkylaryl sulfonate detergents which find the widest usage in household, commercial and industrial consumption. Another large class of detergents based upon the alkylaryl portion of the molecule are the oxyalkylated phenol derivatives in which the phenol base may be prepared from an alkyl hydrocarbon. Still another class of detergents derived from alkylaryl hydrocarbons are the polyoxyalkylated aniline and alkylaniline derivatives of the alkylate which are water-soluble products and are formed by nitrating the alkylate, catalytically reducing the resulting nitro-substituted alkylate to form the amine and thereafter polyoxyalkylating the amine to form the resulting detergent product. Still other products having an alkylaryl base are widely known in the arts, although alkylaryl sulfonates provide the largest single source of stream pollution and therefore constitute the largest single product of ultimate use from the alkylate product of this invention. The term: "aryl" as intended herein refers to a monocyclic aromatic nucleus which may be hydrocarbon or may contain various nuclear radicals as substituents, such as, for example, hydroxyl and amino.

In the present process for the production of alkyl-substituted aromatic hydrocarbons, utilizable as charge stocks in the production of biologically soft surface active agents and particularly water-soluble detergents, the source of the alkylating agent to provide the alkyl group on the aromatic nucleus is an important factor in the synthesis of the alkylated product of this process. In order to produce an alkyl aromatic hydrocarbon in which the alkyl group is a long chain group containing from 9 to 15 carbon atoms and having a biodegradable chain structure, the alkylating agent condensed with the aromatic hydrocarbon receptor must also have a biodegradable chain structure. Even if a normal, 1-olefin is utilized as the alkylating agent in the condensation with aromatic hydrocarbon receptor the alkyl chain entering the aromatic nucleus will still have a secondary structure at best.

This secondary structure of the resulting alkylate follows well-established principles of organic chemistry which establish the fact that the entering alkyl chain attaches to the aromatic nucleus on the carbon atom of the mono-olefin chain having the least number of hydrogen atoms and even when 1-olefins are utilized as the alkylating agent, the point of attachment of the entering alkyl chain will be on the number two carbon atom of the olefin chain, as follows:

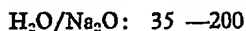
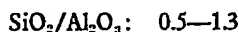
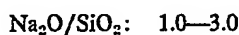


The degree of branching in the alkyl chain of the resulting alkylate will depend upon the degree of branching in the chain of the olefin utilized as the alkylating agent in the above reaction and therefore, normal 1-olefins will produce the least degree of branching of the alkyl chain attached to the aromatic nucleus of the resulting alkylate. It has now been found that one of the preferred sources of normal olefins which, upon alkylation, will yield alkylates in which the alkyl portion of the molecule has the maximum degree of linearity are those normal paraffins which, upon dehydrogenation under controlled conditions to preserve the linearity of the olefinic product, produce an olefin in which the double bond remains between the number one and number two carbon atoms, in the chain, and which are present as straight chain paraffins in a kerosene boiling range fraction containing from 9 to 15 carbon atoms in the paraffin molecule. These paraffins when dehydrogenated in the presence of catalysts which have a minimum of isomerizing activity yield normal or straight chain 1-olefins capable of yielding alkylates upon alkylation in which the alkyl group has the maximum degree of linearity.

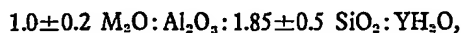
Any suitable source of normal paraffins, of course, may be utilized for supplying the feed stock to the separation stage of the present process, including an appropriately boiling fraction of a straight run petroleum distillate, or of the products of the Fischer-Tropsch reaction which includes paraffinic hydrocarbons in the C_9 - C_{15} range formed by the hydrogenation of carbon monoxide in the presence of a catalyst of the iron group metals, the hydrogenated products of ethylene polymerization which includes paraffins having from 9 to 15 carbon atoms, the hydrogenated fatty acids

which upon complete reduction produce paraffinic hydrocarbons having straight chain configuration, as well as other sources of such paraffinic compounds, all contemplated herein as a source of feed stock to the present process. Although any of the foregoing sources of normal paraffins may be utilized herein as the primary feed stock in the present process, the least costly and generally preferred source of normal paraffins is the kerosene boiling range fraction boiling within the range of from about 170° to about 240°C. containing the desired C₉—C₁₅ paraffins which upon conversion to an olefin-acting derivative, followed by condensation with an aromatic compound provide a hydrocarbon radical of sufficient hydrophobic activity to yield the hydrophobic portion required in the structure of the detergent molecule. In all of the foregoing sources of straight chain paraffins, however, a significant proportion of branched chain isomers occurs in admixture with the normal paraffins, which isomers, if converted to their olefin-acting analogs do not yield the desired alkylates having a biodegradable alkyl group. Consequently, in order to produce an alkylate product having the maximum degree of linearity and the most advantageous properties insofar as its biological degradability is concerned, the paraffin feed stock to the olefin production step of the present process must be subjected to a separation procedure in order to segregate and isolate the components of the paraffinic mixture having the desired straight chain structure, as hereinafter described.

The separation and recovery of the normal paraffins from the hydrocarbon fractions containing them is based upon a method of separation which selectively differentiates between normal and isoparaffins and between normal and cyclic paraffins and thus requires a molecule sieve type separation process in which the separating agent is selective for the normal components, present in the mixture of paraffinic isomers. Several molecular sieve type separation procedures are available which have sufficient selectivity to provide product streams of at least 95 percent normal paraffin purity. One of the preferred separating agents having this degree of selectivity is a molecule sieve sorbent characterized by its chemical composition as a dehydrated metal aluminosilicate having a zeolite structure in the crystals of aluminosilicate and containing pores of about 5 Ångstrom units in cross-sectional diameter which are of sufficient size to permit the entry of paraffinic or olefinic aliphatic compounds, but are not of sufficient size to permit the entry of branched chain or cyclic compounds. The metal constituent of these zeolitic compositions is selected from the alkaline earth metals, preferably calcium or magnesium which are not only the most effective but also the least expensive of the various alkaline earth metal derivatives. These molecular sieve type sorbents which are prepared by the selective crystallization of the metal aluminosilicate from aqueous solutions of water glass or other suitable source of silica sol, a source of alumina or aluminum hydroxide, and an alkali metal hydroxide and containing certain specific proportions of these oxides, as well as water, are prepared by combining water, sodium silicate (as "water glass") or sodium-free silica sol or an alcohol ester of silicic acid such as ethyl ortho-silicate, alumina or an alkali metal aluminate and sodium hydroxide in proportions sufficient to provide the following ratios of reactants, indicated as their oxides:



and heating the aqueous mixture at a temperature of from about 40° to about 120°C. for a period up to about 40 hours or until crystal formation is complete, depending upon the temperature of the reaction. The crystals which precipitate are the sodium form of the metal aluminosilicate and have the following empirical composition:



where M is sodium, if the sodium derivatives are involved in the preparation although any of the alkali metals may also be utilized, and Y has a value up to about 6. The calcium or other alkaline earth derivatives (having pore diameters of about 5 Ång-

strom units, required in the present process) of the above alkali metal salts are prepared by ion-exchange of the alkali metal from the above zeolites with a water-soluble alkaline earth metal salt, such as an aqueous calcium chloride solution. The resulting hydrated crystals of the alkaline earth aluminosilicate are thereafter dried and calcined at temperatures of from about 150° to about 500°C. to dehydrate the water of crystallization and thereby develop pores having the required diameter of about 5 Ångstrom units, in which form the product is activated as a molecular sieve for the present separation process.

Another class of separating agents which are selective for normal compounds, including olefins if present in the hydrocarbon mixture, is urea which separates these components by the formation of an adduct or clathrate of the urea with the straight chain compound. Thus, urea crystals or an aqueous solution of urea is mixed with the hydrocarbon fraction at a temperature of from about -10° to about 35°C., the crystalline adduct forming immediately as the urea is mixed with the hydrocarbon fraction from which the normal components are to be separated, the crystals being filtered from the remaining liquid and thereafter separately decomposed by increasing the temperature of the separated crystals or by displacing the normal hydrocarbon bound to the urea in the form of the clathrate with a preferentially sorbed compound, such as an alcohol, including methanol, ethanol, normal propanol, etc., an aldehyde such as propionaldehyde, acetaldehyde, etc., or other aliphatic compound containing a polar radical.

The straight chain hydrocarbon present in the mixture of hydrocarbon isomers may also be separated from the cyclic and isoparaffinic components present in the mixture by contacting the mixture with thiourea which selectively forms adducts with the branched chain and cyclic components, leaving the normal hydrocarbons present in the mixture as a raffinate stream which may be withdrawn from the clathrate formed between the thiourea and the cyclic or isoparaffinic components. Separation procedures utilizing the above separating agents are well-known in the prior art and further reference thereto may be had for specific details of the process techniques.

The straight chain aliphatic hydrocarbon separated from the mixture of hydrocarbon isomers boiling in the kerosene range by the above-described separation process is, in accordance with the present combination process, subjected to a dehydrogenation reaction at dehydrogenation reaction conditions and in the presence of a suitable dehydrogenation catalyst which will result in the production of a mono-1-olefin of the same number of carbon atoms as the initial paraffinic stock and of the same straight chain structure as the charge stock; that is, without isomerization to a branched chain structure.

The n-paraffins are thereby converted to mono-olefins which undergo condensation with an aromatic compound containing a nuclearly replaceable hydrogen atom to form the present alkylate product. In an alternative method of synthesizing the alkylate recovered from the paraffinic feed stock the normal paraffin is converted to an olefin-acting compound which is thereafter condensed with the aromatic reactant to form the present alkylate product. Thus, the n-paraffin is first subjected to halogenation, for example, by reacting chlorine with the liquid n-paraffins until mono-halogenation is complete and thereafter the resulting alkyl chloride is condensed with the desired aromatic hydrocarbon in the presence of anhydrous aluminum halide, such as aluminum chloride, at reaction conditions in which hydrogen halide is released and the mono-alkylate formed by the condensation of the aromatic hydrocarbon with the alkyl halide is formed. In this condensation the n-alkyl halide formed by halogenation of the n-paraffins, when contacted with the aromatic hydrocarbon in the presence of the aluminum halide acts in the same capacity as the corresponding olefin in the presence of an alkylation catalyst, the halogen radical of the halide combining with the replaceable hydrogen atom on the nucleus of the aromatic hydrocarbon to form hydrogen halide and the free bond on the alkyl residue combines with the free bond on the aryl nucleus to form the alkylate. The term "olefin-acting" reactant as used herein is intended to refer to the olefin itself formed by dehydrogenation of the paraffin or to the alkyl halide formed by halogenating the n-paraffin.

The conversion of the straight chain paraffins recovered by the above separation procedure from the mixture of aliphatic and/or cyclic hydrocarbons to their mono-olefinic analogs by dehydrogenation is effected at temperatures of from about 450° to about 600°C. in the presence of a particular type of catalyst which is especially suitable for this conversion without isomerization of the normal paraffins to their branched chain isoparaffin analogs, thereby maintaining the straight chain character of the product to correspond to that of the paraffinic hydrocarbon feed stock. Suitable

5 catalytic agents which minimize the isomerization of the aliphatic feed stock and/or olefinic product are the neutral oxides of the elements of Group VI of the Periodic Table, preferably the oxides of chromium, molybdenum, tungsten and uranium deposited on an inert support, especially a support free of acidic ions, and more preferably, alumina, the composite containing from 0.5 percent, up to about 20 percent by weight of the Group VI metal oxide, and more preferably from about 2 percent to about 10 percent thereof. Particularly preferred catalyst compositions are the composites of alumina-chromia containing from 5 to about 12 percent chromia and alumina-molybdena containing from 2 to about 20 percent of molybdena. The above composite catalysts of this type may contain from 1 to about 10 percent by weight of an alkali metal oxide, such as potassium or lithium oxide. 10

The dehydrogenation reaction is preferably effected at relatively short contact periods between the catalyst and feed stock paraffins and at pressure in the region of atmospheric pressure. Thus, the contact time of the feed stock with the catalyst may be a relatively short period of time, at a rate of flow corresponding to a liquid hourly space velocity of from about 0.1 to about 2.0 volumes of liquid per volume of catalyst per hour. In the preferred method of operation, the dehydrogenation reaction is effected in the absence of hydrogen, although hydrogen may be added to the feed stock in order to reduce the deposition of carbon on the catalyst during the reaction. 15 In general, the conversion of the normal paraffin charge stock to the mono-olefin analog corresponding thereto does not go to completion in a once-through passage of the charge stock through the catalyst bed and in order to increase the concentration of mono-olefin in the dehydrogenation product, it is usually preferred to separate the mono-olefins from the unconverted normal paraffins and recycle the latter back to the dehydrogenation zone. The separation of the mono-olefin product from the unconverted paraffins may generally be effected by passing the dehydrogenation reaction product in liquid phase through a bed of a suitable adsorbent which selectively retains the olefinic component on the surface of the adsorbent without adsorbing the normal paraffin. Suitable adsorbents of this type include silica gel particles, activated charcoal (such as coconut shell char), activated alumina (such as calcined bauxite) and others. Solvent extraction may also be utilized to effect the separation of the mono-olefins from the paraffins contained in the dehydrogenation reaction effluent, utilizing solvents such as methyl alcohol, phenol, ethylene glycol, diethylene glycol, aqueous copper- and silver phosphate solutions, or other solvents well-known in the prior art. It is to be emphasized that all dehydrogenation catalysts known in the dehydrogenation art will not operate to produce the desired mono-olefin in which the double bond is in the 1-position upon contact of the normal paraffin with the catalyst at dehydrogenation conditions. Thus, dehydrogenation catalysts containing an acidic component in the support such as catalyst supports containing combined chloride ions or other halogen ions in a fixed form in the catalyst composition not only effect the desired dehydrogenation, but also cause isomerization of the normal paraffins to various branched chain structures, which upon subsequent alkylation and conversion of the resulting alkylate to detergent products yield materials which have an alkyl chain of branched chain structure possessing the aforementioned resistivity to bacteriological degradation. Isomerization of long-chain paraffin hydrocarbons results in the production of various isomers of all degrees of branching and all manner of position isomers which upon dehydrogenation and subsequent alkylation of the aromatic nucleus would yield alkylates having branched chain alkyl groups. Therefore, the catalyst compositions designated hereinabove, and particularly the preferred alumina-chromia and alumina-molybdena composites are especially desirable for effecting the dehydrogenation step of the present process. 25 30 35 40 45 50

Following dehydrogenation of the normal paraffins and their recovery from the mixed dehydrogenation product as a relatively pure 1-olefin concentrate, the mono-olefin is utilized as an alkylating agent for an alkylatable, mono-cyclic aromatic hydrocarbon or phenol selected from the group consisting of toluene, benzene, xylene, ethylbenzene, methylethylbenzene, and phenol, yielding a mono-alkylate which is the desired end product of the present process. The alkylation reaction is preferably effected in the presence of a suitable catalyst capable of promoting the condensation reaction, generally an inorganic material characterized as an acid-acting compound which catalyzes the alkyl transfer reaction involved in the process. Acid-acting inorganic compounds having alkylating activity include certain mineral acids, such as sulfuric acid containing not more than about 15 percent by weight of water and preferably less than about 8 percent by weight of water, including used sulfuric acid catalysts recovered from the alkylation of isoparaffins with mono-olefins, hydrofluoric acid of at 55 60

least 90 percent concentration and containing less than about 10 percent by weight of water, liquefied anhydrous hydrogen fluoride, anhydrous aluminum chloride or aluminum bromide, boron trifluoride (preferably utilized in admixture with concentrated hydrofluoric acid) and other acid-acting catalysts, particularly of the Friedel-Crafts class of metal halides. The catalyst particularly preferred for the present alkylation reaction is hydrogen fluoride containing at least 85 percent and more preferably at least 98 percent hydrogen fluoride. Sulfuric acid of at least 88 percent concentration, up to 100 percent, is also a preferred catalyst. In the process of condensing the aromatic compound with the mono-1-olefin, the hydrogen fluoride, for example, in liquid phase and the aromatic compound are charged into a stirred pressure autoclave, followed by the addition to the stirred mixture of the mono-olefinic hydrocarbon, the resulting mixture being thereafter maintained, as the stirring continues, at a temperature of from about $-20^{\circ}\text{C}.$ to about $30^{\circ}\text{C}.$ In order to maximize the production of alkylate from the mono-olefin charged to the process, it is generally preferred that the molar ratio of aromatic compound to the olefin reactant charged into the alkylation reaction be greater than 1:1, more preferably within the range of from about 2:1 to about 15:1 moles of aromatic per mole of olefin. The effluent mixture is separated to recover the organic portion of the reaction effluent from the used catalyst, and the organic mixture is thereafter fractionated to recover the excess aromatic hydrocarbon from the residue of alkylaromatic product which remains in the distillation zone as a higher boiling residue. In most instances, when the molar proportion of aromatic to mono-olefin charged to the process exceeds 1:1 and more desirably from about 5:1 to about 10:1, the mono-olefin is more or less completely consumed during the condensation reaction and a mono-alkylate rather than a poly-alkyl-substituted aromatic alkylate is obtained as the principal product of the process.

As indicated above, the n-paraffin recovered from the mixed paraffin feed stock is also capable of providing the source of the alkyl group in the final detergent product by converting the n-paraffin to an olefin-acting n-alkyl halide and condensing the resulting halide with the aromatic reactant involved in the present process. The condensation of the aromatic reactant with the alkyl halide in many cases constitutes the preferred manner of obtaining the alkylate. Thus, the n-paraffin is first converted to its mono-halide derivative by adding the halogen (preferably, chlorine or bromine) of the n-paraffin at a temperature which results in the substitution of a single halogen atom for one of the hydrogen atoms in the paraffin chain. For example, chlorine is bubbled into the n-paraffin maintained at from about 10° to about $50^{\circ}\text{C}.$ until mono-halogenation is complete, depending upon the average chain length of the paraffins contained in the n-paraffin mixture. In most instances the halogenation results in the formation of an n-alkyl halide (that is, the halogen substitution product in which the chlorine occupies the number 1 carbon atom). Thereafter, the resulting alkyl halide is condensed with the aromatic reactant by mixing the alkyl halide with the aromatic reactant and adding to the mixture an anhydrous aluminum halide selected from aluminum chloride and aluminum bromide in an amount of from 2 percent to about 20 percent (preferably from 5 to about 10 percent) by weight of the alkyl halide while maintaining the temperature at from about -10° to about $50^{\circ}\text{C}.$ In this condensation reaction an excess of the aromatic reactant (from 2 to 1 to about 15 to 1 moles of aromatic per mole of alkyl halide) is utilized in order to promote the formation of mono-alkylate, rather than polyalkylate, and the excess aromatic hydrocarbon is recovered from the reaction mixture by distillation.

The alkylate obtained by one of the aforementioned condensation reactions constitutes the raw material or starting stock for the preparation of the ultimate detergent or surface active product. Thus, a highly effective detergent is prepared from the alkylate by sulfonation which produces the mono-sulfonic acid derivative, followed by neutralization with a salt-forming base such as sodium hydroxide to form a water-soluble alkyl-aryl sulfonate detergent. The alkylate may also be nitrated to form a nuclearly-substituted mono-nitro derivative which is catalytically reduced to the mono-amine-substituted analog. This amine is thereafter condensed with ethylene oxide or propylene oxide to form the corresponding polyoxyalkylated detergent product, preferably containing from 10 to about 15 oxyalkylene units. In the case of the phenol alkylates, these are converted directly to detergent products via oxyalkylation with ethylene or propylene oxide (preferably, ethylene oxide) until the product contains from 6 to about 15 oxyethylene units per molecule.

The present invention is illustrated in the following examples.

EXAMPLE I.

In the following comparative preparations a straight-run petroleum fraction is used which has been obtained from Pennsylvania crude oil and boils within the range of 170° to 220°C. and has the following composition according to general classes of hydrocarbons:

C ₁₁ —C ₁₅ Aliphatic paraffins:	73%
C ₉ —C ₁₅ Naphthenes	: 24%
C ₈ —C ₁₅ Aromatics	: 3%

This fraction is resolved into the following two classes of components (1) straight chain or normal paraffins and (2) a mixture of isoparaffinic and cyclic hydrocarbons, the recovered normal paraffins are thereafter dehydrogenated to their mono-olefin analogs and these are thereafter used to alkylate benzene, the recovered benzene alkylate is sulfonated, followed by neutralization of the resulting sulfonic acid to the alkylaryl sulfonate salt. This product is then compared (as to detergency and biological softness) to the corresponding sulfonate salt of the alkylate formed by alkylating benzene with the mixture of branched chain olefins contained in a propylene tetramer fraction boiling from 170 to about 225°C.

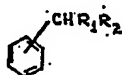
The normal paraffins in the straight-run fraction are separated therefrom by contacting the mixture with pelleted calcium alumino-silicate molecular sieves (Linde Air Products Co., 5A molecular sieves). For effecting this separation, the straight-run kerosene fraction is poured at room temperature (25°C.) into a vertical column packed with the sieves and of sufficient capacity to provide a column of sieves 1.542 meters in length containing 107.6 liters of the 5A sieve particles, each particle having a dimension of approximately 3.2 mm × 3.2 mm. A raffinate effluent from the bottom of the column of sieves consists of n-paraffin-free-hydrocarbon. The normal paraffin components of the kerosene fraction (about 73% of the total volume of kerosene) remain within the column sorbed on the sieve particles. The residual raffinate occupying the surface of the sieve particles is removed from the column by washing the sieves with isopentane which can be subsequently separated from the products by distillation.

After completely draining the column of isopentane wash, the sorbed n-paraffins removed from the kerosene feed stock are desorbed by filling the column with liquid n-pentane at 25°C., allowing the n-pentane to displace the kerosene-derived n-paraffins sorbed on the molecular sieves by the Mass Action effect and after 10 minutes the liquid surrounding the sieve particles is drained into a distillation flask receiver. The column is again filled with n-pentane and after standing for an additional 10 minutes, the liquid in the column is drained into a second distillation flask. Distillation of the n-pentane from the effluent stream in each case left a residue of kerosene n-paraffins (98 percent normal components of C₁₁—C₁₆ chain length) in each flask, 96 percent of the entire residue being in the first flask.

The n-paraffins recovered from the kerosene fraction in the above run are thereafter subjected to dehydrogenation by passing them through a small pilot plant dehydrogenation reactor consisting of a vertical steel pipe of 0.9144 meters in length packed with an alumina-chromia catalyst containing 12 percent by weight of chromium oxide and jacketed with a thermostatically controlled electric heating element which maintained the catalyst bed at 520°C. and at atmospheric pressure during the passage of the paraffinic charge stock through the bed of catalyst at a liquid hourly space velocity rate of 1.2 volumes of charge per volume of catalyst per hour. The product effluent from the bottom of the reactor is cooled and liquefied in a water-cooled condenser, the non-condensed gasses being withdrawn overhead from the condenser. A yield of mono-olefin representing 73 percent by weight, based on the normal paraffin charged is recovered from the total product. The olefin product which is made up of various double-bond position isomers is separated from unconverted paraffins by passing the liquid dehydrogenation product through a column of activated silica gel particles, the olefinic component being retained by the silica gel and the paraffins passing through the column as raffinate. The olefins are recovered from the silica gel by displacement of the mono-olefin adsorbate with benzene, a preferentially adsorbable compound.

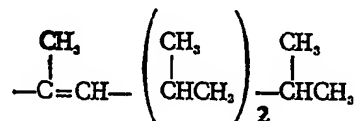
The n-olefins as recovered by the above procedure are then mixed with 10 molar proportions of benzene, based on the average molecular weight of the olefins as 168 (dodecene) and the hydrocarbon mixture cooled to 0°C. as enough hydrofluoric acid of 98.5 percent concentration is added (with stirring) to provide a weight ratio of acid to olefins of 1.5. The mixture is maintained within the temperature range of from 0—10°C. during a period of one hour after which the mixture is allowed to settle and the lower acid layer withdrawn from the upper hydrocarbon layer. The hydrocarbon phase is then washed with dilute caustic to remove dissolved hydrogen fluoride and then distilled to remove excess benzene and a small quantity of aliphatic hydrocarbons boiling in the mono-olefin range. The residue, consisting of 96 percent mono-alkyl-benzenes represents an 82 percent by weight yield of alkylate, based upon the olefins charged.

The alkylate product, when subjected to infra-red analysis consists of secondary alkylbenzenes of the following structure:



in which R₁ and R₂ are normal alkyl radicals of from 1 to 13 carbon atoms in chain length and in which R₁ + R₂ is from 9 to 14, a predominant proportion of the product being of the structure in which R₁ is methyl and R₂ is n-tridecyl.

A second sample of alkylate is prepared by alkylating benzene with a so-called propylene tetramer fraction boiling from 170° to 225°C. in accordance with the same procedure specified above for the n-olefin alkylate production. Propylene tetramer consists of a mixture of isomers and homologs all of which are of branched chain structure of the following type:



Each of the alkylates prepared as indicated above is sulfonated by mixing the alkylate with an equal volume of liquefied n-butane and then with 30 percent oleum added to the diluted alkylate mixture as a small stream flowing onto the chilled surface of a rotating cylinder, the surface of the cylinder being cooled by circulating salt water cooled to -10°C. on the inside of the cylinder as the latter is rotated, scraped and the mixture re-spread on the surface of the cylinder by a stainless steel blade, the n-butane evaporating into a hood as the heat of reaction raises the temperature and boils off the butane, thereby maintaining the temperature at or near 0°C.

The sulfonation reaction mixture is diluted by mixing with ice and thereafter the acids are neutralized to a pH of 7 with sodium hydroxide. Both products are light cream-colored solids which are completely soluble in water. The evaporated solids are extracted with 70 percent ethanol to recover sodium sulfate-free products and thereafter are mixed with sufficient sodium sulfate builder salt to provide detergent compositions containing a 60—40 wt. ratio of sodium alkylaryl sulfonate and sodium sulfate. Each composite product when tested for detergency in a standard Launder-O-Meter test procedure removed a synthetic soil composition from cotton cloth (muslin swatches). The product prepared from the propylene tetramer alkylate is rated as about 112 percent as effective as pure sodium oleate, and the product prepared from the n-olefin alkylate is about 114 percent as effective as the standard sodium oleate at equal concentrations, using water of 71°C. as the solvent in the detergent solution and measuring the effectiveness of the detergent by determining the reflectance of white light from the swatch samples laundered in the detergent solution and comparing the reflectance therefrom with a sample laundered in sodium oleate solution.

Samples of each of the above detergent preparations are separately subjected to simulated sewage treatment conditions in order to determine the relative rates and

5 extent of removal of each of the samples from a synthetic sewage mixture of known composition. A 0.3 percent aqueous solution of each of the above detergents (378.5
liters each) is prepared and to each of the solutions 0.227 kg of urea (to supply nitro-
gen nutrient), 0.091 kg of sodium sulfate (to supply $-\text{SO}_4$ nutrient), 0.091 kg of
10 potassium phosphate (to supply $-\text{PO}_4$ nutrient) and trace quantities of zinc, iron,
magnesium, manganese, copper, calcium and cobalt are added to provide the necessary
nutritional requirements of the bacteria added to each of the solutions in the form
of 0.4536 kg of activated sewage sludge supplied from a sewage treatment plant.
The simulated sewage composition placed in a large circular tank is thereafter stirred
15 as air is introduced into the bottom of the tank in the form of fine bubbles through
fitted glass nozzles. Approximately 50 cc. samples of the sewage suspension are
removed from each of the tanks at three-hour intervals after an initial digestion of 24
hours, filtered, and equal quantities of the filtrate (50 cc.) are measured into shaker
bottles to determine the height of foam produced after shaking each of the samples
20 of filtrate under similar test conditions. 50 cc. samples of each of the initial, non-
digested detergent solutions, shaken for 10 minutes in the test apparatus produced
essentially equal volumes of foam, 15 cm. in height. For each of the solutions sampled
thereafter, the results of foam height determinations which are an empirical measure
of the amount of detergent remaining in solution, are presented in the following
Table I for each of the samples:

TABLE I

QUANTITY OF FOAM PRODUCED FROM 50CC. SAMPLES OF SEWAGE
SOLUTION AT VARIOUS INTERVALS OF SEWAGE TREATMENT TIME

Sample No.	Time of Treat- ment, Hrs:	Foam Height, Cm.	
		Propylene Tetramer Alkylate	Straight Chain Olefin Alkylate
1	0	15	15
2	24 + 3	14	13
3	24 + 6	14	12
4	24 + 9	13.5	10
5	24 + 12	13	8
6	24 + 15	13	7
7	24 + 18	12.5	6
8	24 + 24	11.5	5
9	48 + 6	11	4
10	48 + 12	10.5	2
11	48 + 24	10	1

The sample of detergent prepared from the branched chain (tetramer) alkylate remains active (i.e., produced foam) even after 108 hours.

EXAMPLE II.

25 A run similar to the above, but utilizing detergent prepared by oxyethylating phenol alkylates, one sample of which contain a C_{12} alkyl group derived from propylene tetramer and the other sample of which is a C_{12} alkyl group derived from a normal olefin produced by dehydrogenation of a normal paraffin separated from a straight-run naphtha yielded results of essentially the same character as the results

25

shown in Example I, above, in that the detergent product prepared from the alkylate produced from the dehydrogenated normal paraffin is also biologically degradable to a more pronounced degree than the branched chain olefin alkylate product.

WHAT WE CLAIM IS:—

- 5 1. A process for producing an alkylaryl compound suitable for the preparation of a biologically soft detergent product therefrom in which the aryl nucleus is mono-cyclic and the alkyl radical on the aryl nucleus is an alkyl group containing from 9 to 15 carbon atoms characterized in that a straight chain paraffin of at least 95% normal paraffin purity is separated from a paraffinic naphtha boiling in the range of 10 from 125° to 250°C. by a selective separation treatment of the group consisting of molecular sieve sorption, urea adduct formation and thiourea adduct formation, the separated straight chain paraffin without intentional isomerization of the straight chain structure is converted to an olefin-acting derivative of the group consisting of 15 mono-olefinic hydrocarbons and alkyl halides having the same carbon atom number as said straight chain paraffin and an aromatic compound selected from the group consisting of benzene, toluene, xylene, ethylbenzene, methylethylbenzene, and phenol is alkylated with said olefin-acting derivative to form the mono-alkylate of said aromatic compound.
- 20 2. The process according to claim 1, characterized in that the straight chain paraffin recovered from the paraffinic naphtha is converted to a mono-olefinic hydrocarbon by dehydrogenating the normal paraffin in the presence of a non-acidic dehydrogenation catalyst.
- 25 3. The process according to claim 2, characterized in that said dehydrogenation catalyst is an alumina-chromia composite containing an alkali metal oxide.
4. The process according to claim 1, characterized in that the separated normal paraffin is converted to an olefin-acting alkyl halide by halogenating said paraffin with a halogen selected from the group consisting of chlorine and bromine and thereafter the resulting alkyl halide is condensed with said aromatic compound in the presence of a catalyst selected from the group consisting of aluminum chloride and aluminum bromide. 30
5. The process according to one of the claims 1 to 4, characterized in that the straight-chain paraffinic hydrocarbon of at least 95% normal paraffin purity is separated from a straight-run hydrocarbon distillate boiling in the range of from 170° to 240°C.
- 35 6. The process for the production of an alkylaryl compound suitable for the preparation of a biologically soft detergent product therefrom substantially as described.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2.
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1965. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.